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A Thiodiethane Thiol Modified Silica Coated Magnetic Nano Particles for Preconcentration and Determination of Copper (II), Nickel(II) and Cobalt (III) in Environmental and Food Samples

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ABSTRACT

New magnetic adsorbent, 2,2-thiodiethanethiol grafted with tetraethyl orthosilicate modified Fe₃O₄ nanoparticles, was developed for separation and preconcentration of Cu^{II}, Ni^{II} and Co^{II} in environmental and food samples. The concentrations of Cu^{II}, Ni^{II} and Co^{II} were determined by inductively coupled plasma– Atomic emission spectrometry. A comprehensive study on the factors affecting the extraction and desorption efficiencies was performed under optimized conditions, the method was linear in the 0.1–900 ng mol L⁻¹ range (before preconcentration) with detection limits of 3,7 and 3 ng L⁻¹ for Cu^{II}, Ni^{II} and Co^{II} respectively. Relative standard deviations of 2.5, 2.7 and 2.2% (concentration 50 ng mol L⁻¹, n/47) and high preconcentration factors of 291, 285 and 288 were also obtained. The accuracy of the proposed method was validated by analyzing a water certified reference material with satisfactory recoveries. The method was successfully applied for the determination of analytes in River waters and canned Mosu fish samples.

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1. Introduction

Recent advances have been devoted for the progressively growing field of nano-technology and nanoscience in the last two decades. Design of novel nano-materials is also a subject of research interest in recent years. Magnetic nano materials are representing an important class of Compounds that are known by their unusual characteristics as well as multidiscipline applications.¹⁻³The high interests in magnetic nano materials are mainly related to their direct and simple separation from their matrices by the action of an external magnetic field. Magnetic nano materials are also considered as potential adsorbents due to their high surface area and excellent chemical selectivity.⁴⁻⁶ Moreover, water

pollution is considered to be a major environmental problem worldwide and among the various water pollutants, heavy metals require special attention because of their toxic effect on humans and the environment.⁷ Heavy metals are considered to be the most important pollutant in source and treated water and the increased use of heavy metals industrially resulted in an increase in the availability of metallic substances in natural source water.⁸ Apart from that, heavy metals form a very dangerous category due to their toxic and carcinogenic nature, non biodegradable and hence tend to accumulate in the environment for long time. Some of these toxic elements are cadmium, lead, mercury, nickel, chromium and zinc.⁹

Magnetic nanoparticles that exhibit very large specific areas are very promising supports for the development of an efficient magnetic

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separation process.¹⁰⁻¹¹ So many publications have been reported for the synthesis of modified magnetic nanoparticles as adsorbents to exploit their applications for metal ion determination. Yuwei¹² reported magnetic chitosan nanoparticles for the removal of Cu(II) ions from aqueous solutions. Faraji *et al.*,¹³ used decanoic acid coated magnetic nanoparticles for extraction of some metal ions in water samples by ICP-OES. Wang *et al.*,¹⁴ reported an extraction and preconcentration procedure for the determination of trace levels of cobalt using alumina coated magnetic nanoparticles by a sequential injection system with detection by electrothermal atomic absorption spectrometry. Coating of magnetic nanoparticles with silica is a commonly used procedure to obtain magnetic sorbents owing to its stability and versatility of surface modification. Huang¹⁵ Although reported 2,20-thiodiethanethiol and its derivatives exhibited excellent selectivity toward Ag^{II} ions as an ion-selective electrode.¹⁶ According to the literature survey, no preconcentration study has been performed using thiodiethanethiol modified silica coated magnetic nanoparticles for determination of metal ions.

Present study, an extraction/preconcentration procedure using thiodiethanethiol modified tetraethyl orthosilicate coated Fe₃O₄ nanoparticles was used for the determination of Cu^{II}, Ni^{II} and Co^{II} ions in environmental and food samples and the metal ion concentrations were measured using ICP- AES. The optimization of preconcentration step was performed by studying the main parameters affecting the extraction preconcentration efficiencies and the proposed method showed high potential for effective extraction of ultra-trace amounts of Cu^{II}, Ni^{II} and Co^{II} in water and food (Mosu fish) samples

2. Materials and Methods

2.1. Apparatus

Cu^{II}, Ni^{II} and Co^{II} measurements were performed with a Varian Vista-Pro ICP-OES (Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The operating conditions are summarized in Table 1. High purity argon was used as the carrier gas for mercury vapor introduction to the cell. Scanning electron microscopy (SEM) of the modified magnetic nanoparticles was performed by ZEISS scanning electron microscope with an acceleration voltage of 20 kV. The pH of the solution was measured using a Elico Li pH meter with a combined (glass/calomel) electrode.

2.2. Reagents and Solutions

All chemicals and reagents were of analytical grade and the presence of target metal ions was not detected within the working range. Ferric chloride hexahydrate (FeCl₃.6H₂O), ferrous chloride tetrahydrate (FeCl₂.4H₂O), sodium chloride, tetraethyl orthosilicate, glacial acetic acid, methanol, ammonia solution (25% w/w), glycerol, chloroform and acetonitrile were purchased from Merck (Darmstadt, Germany). Stock solution was prepared by appropriate dilution of ICP standards of Cu^{II}, Ni^{II} and Co^{II} (Merck, Germany). Thiodiethanethiol was purchased from Sigma and double distilled water was used throughout the experiments.

Stock standard solutions of the analytes (1000 mg mol L⁻¹) were prepared by dissolving their nitrate salts in deionized water. The working solutions were prepared daily by appropriate dilution of stock solutions with deionized water. Other metal ions stock solutions (1000 mg mol L⁻¹) were prepared from their nitrate or chloride salts by conventional methods. A solution of 1.0% (v/v) thio diethane thiol was prepared by dissolving an appropriate volume in 75mL methanol and then diluting the solution to 150 mL with deionized water. Eluting solution was prepared by dissolving 2.5 g of thio urea [to give a 5% (w/v) solution] in 50mL of 1.0M HCl and prepared daily.

2.2.1. Preparation of Magnetic Adsorbents

Magnetic Fe₃O₄ nanoparticles were synthesized according to a simple method described in the literature (C. Huang and Hu 2008; Guihen and Glennon 2003; Mashhadizadeh and Amoli-Diva 2013) by alkaline co-precipitation of an aqueous mixture of Fe₂þ and Fe₃þ with concentrated ammonium hydroxide. Briefly, FeCl₂ 4H₂O (4.3 g) and FeCl₃. 6H₂O (11.6 g) were dissolved in 200mL deionized water under a nitrogen atmosphere with vigorous stirring at 85°C. An ammonia solution (40mL, 25% w/w) was then added. The resulted magnetic precipitate was separated from the solution by placing a super magnet on the bottom of the beaker and the supernatant was removed by decantation. The precipitate was washed with deionized water (200 mL, three times) and 0.02M sodium chloride (100 mL, twice). The washed magnetic nanoparticles were transferred into a 250mL round bottom flask and allowed to settle. The supernatant was removed and 80mL of 10% (v/v) tetraethyl orthosilicate followed by 60 mL glycerol were added. The mixture was then stirred under a nitrogen atmosphere at 90°C for 2h and cooled to room temperature. The suspension was washed sequentially with deionized water (200mL, three times), methanol (100mL, twice), and deionized water (200mL, twice). The prepared silica coated magnetic nanoparticles were isolated by magnetic decantation and 150mL of 1.0% (v/v) thiodiethanethiol were added to the suspension. The mixture was sonicated for 2h. The resulting adsorbent Scheme and XRD showed Figure1.(a,b) was washed under the same conditions as silica coated magnetic nanoparticles and dried in an oven at 45°C.

2.2.2. General SPE Procedure

The recommended procedure for the batch extraction technique was depicted in Figure 2. A portion of sample solution containing 5 mg of each target ion was transferred into a 500mL beaker. The pH value was adjusted to 6 with 0.1M HNO₃ and 0.1M NH₃ solutions and the solution was diluted to a final volume of 300 mL with deionized water. The 85 mg of the adsorbent were added and the solution was stirred for 10 min to facilitate the adsorption of metal ions on the adsorbent surface. The adsorbent was isolated easily and quickly by applying an external magnet and the supernatant was removed. 1mL of 5% (w/v) thiourea in 1.0M HCl was added as the eluent and the suspension was sonicated for 5 min. Finally, a super magnet was used to settle the adsorbent and the elute was transferred into a test flask for subsequent determination. Calibrations were performed against aqueous standard solutions submitted to the same extraction procedure and blank solutions were analyzed in the same manner as standard and sample solutions using distilled water.

2.2.3. Sample Preparation

Tap water samples were collected from various places in and around Tirupati, A.P, India. The samples (150 mL) were stored at 0-5°C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no.41 and clean solution is collected into 250 mL beaker. The contents were diluted up to the mark with double distilled water. 15 mL of this solution is further diluted to get working solution for determination of Cu^{II} as described in above procedure. Before analysis, 10mL of 1.0M K₂S₂O₈ was added to the samples to eliminate Cl⁻ ions interferences and the samples were heated at 80°C for 20 min. The proposed procedure was then performed under the optimum conditions.

The whole Mosu fish samples were homogenized completely using a mixer and then 0.5 g of each sample was digested with 6.0mL of concentrated nitric acid and 5.0mL of 30% H₂O₂ through microwave digestion. Microwave heating was performed on the samples in three successive steps. First, the temperature was increased linearly from 20 to 200°C in 15 min at maximum power; second, the temperature was held at 200°C for 10 min; and finally the samples were cooled to room temperature. 10 mL of 1.0M K₂S₂O₈ were added and the samples were heated at 80°C for 20 min. The digested samples were cooled to the room temperature and an appropriate amount of 1.0M NaOH was

added to neutralize the excess acid. The pH was adjusted to 6 before dilution to 300mL with deionized water and the proposed batch extraction procedure described above was applied. The blank solutions were prepared the same as sample solutions by omitting the samples.

3. Results and Discussion

In general, chemically inert silica network is commonly used as a modifier because it can reduce the particle-particle magnetic bipolar interactions, prevent agglomeration and stabilize Fe₃O₄ nanoparticles (Mashhadizadeh and Amoli-Diva 2013). In addition, it is well known that the most successful selective extractor for soft metal ions is sulfur containing molecules. Thus, in this study thiodiethanethiol grafted tetraethyl orthosilicate modified magnetic nanoparticles were prepared with sulfur atoms which retain soft metal ions such as Cu^{II}, Ni^{II} and Co^{II}. The morphology and size distribution of the prepared adsorbent were characterized by SEM (Figure. 3). Most of the modified MNPs were quasi-spherical in shape and had uniform size distribution with an average diameter of 15–45 nm.

3.1. Effect of pH

The pH value has two effects on the metal ion adsorption. In acidic medium, H⁺ ions can protonate the binding sites of chelating agent and OH⁻ ions may complex or precipitate metal ions in basic medium. Thus, the pH is the first parameter to optimize in any metal ion SPE procedure. In order to determine the effect of pH value on the Cu(II), Ni(II), and Co(II) adsorption on the adsorbent surface, it was varied over a range of 2–10 in the sample solution. The adsorption experiments were performed in triplicate and the results are presented in Figure 4. It can be seen that quantitative adsorption (>90%) was obtained for all target ions in a large pH range of 1-9. At lower pH values, the sulfur atoms in the sorbent can be protonated and the –SH groups can be oxidized if the adsorbent was stored in acidic media for a long time¹⁵, causing a decrease in the adsorption of the analytes. In order to avoid the formation of hydroxide participate at higher pH values, a pH of 6 was employed for subsequent experiments.

3.2. Effect of Desorption Conditions

Magnetic nanoparticles are easily separated from solution by placing an external magnet on the bottom of extraction container. Therefore, no filtration or centrifugation of the sample was needed after extraction. As mentioned before, adsorption of the analyte ions on the magnetic adsorbent occurred at pH > 6 Hence, desorption of the analytes was accomplished by decreasing the pH. Thus, different concentrations of HCl alone and in accompany with some complexing agents (thiourea, thioacetamide, and thiocyanide) were examined. According to the literature, complexing agents improve elution properties of a desorbing solvent¹¹. The experimental results are presented in Figure 5. As can be seen, a mixture of 5% (w/v) thiourea in 1.0M HCl has the best elution efficiency. In addition, the volume of eluent is a important parameter for achieving high preconcentration factors. The eluent volume was varied in the range of 0.5 to 10 mL. The obtained results reveal that 1.0mL of the eluent was sufficient for quantitative desorption of analytes. In addition, desorption time was also evaluated in the range of 2–20 min. The results showed that 5 min is sufficient for quantitative desorption of analyte ions by 1.0mL of 5% (w/v) thio urea.

3.3. Sample Volume

In order to explore the possibility of achieving low concentrations of analyte from large volumes, the maximum applicable volume of sample was determined. The effect of sample volume on the recovery of target ions was studied by applying 25–500mL volumes containing 5 mg of each analyte. The results indicated that the recoveries were quantitative within 25–300mL range. The larger sample volume led to the analyte loss from the sorbent surface. Thus, the sample volume of 300 mL was selected as the optimum volume. The preconcentration factor (PF) was defined as the following equation:

$$PF = \frac{1}{4} \frac{V_s}{V_e} \times R\%$$

Where V_s is sample volume, V_e is eluent volume and R% is the percent recovery. As previously described, 1.0 mL of the eluent was sufficient to eluate the analyte ions from the adsorbent surface; thus, a preconcentration factor of 300 was achieved.

3.4. Effect of Magnetic Nanoparticles Amounts and Extraction Time

Compared with the micron-sized adsorbents, nanoparticles offer a significantly higher surface area and short diffusion routes, which results in high extraction efficiencies and rapid extraction dynamics. The thio diethane thiol grafted tetraethyl ortho silicate modified magnetic nanoparticles adsorbents revealed excellent capability to retain the analytes and quantitative extraction was achieved by using 85 mg of the adsorbents. Furthermore, magnetic nanoparticles were rapidly collected from sample solutions by applying magnetically assisted separation. The extraction time was studied in the range of 2–20 min and the results revealed that 10 min was sufficient for quantitative extraction of the metals. Since the magnetic adsorbents can be completely isolated from the solution in less than 1.0 min, the whole SPE procedure was performed in about 30 min.

3.5. Effect of Co-Existing Ions

The potential interference effects of co-existing ions on the preconcentration and determination of Cu^{II}, Ni^{II} and Co^{II} ions were also investigated. In these experiments, 300 mL of sample solutions with fixed amount (20 mg) of analytes containing the co-existing ions were treated according to the optimized procedure. Table 2 shows the tolerance limits of these ions. As can be seen, the most common cations do not interfere in the determination of target ions. In addition, a number of common anions including Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻ were also tested and the results showed that they did not interfere on the extraction of target ions. However, Cl⁻ interfered in the preconcentration procedure, which may explain by the formation of chlorocomplexes of mercury such as HgCl₂. However, the interference was easily eliminated by adding 10mL of 1.0M K₂S₂O₈ in environmental and food samples during the digestion procedure.

3.6. Adsorption Capacity and Reusability of Adsorbents

The adsorption capacity is one of the important factors which determines how much adsorbent is required to quantitatively remove a specific amount of target ions. The adsorption capacity was studied by a batch procedure. The 85 mg of the adsorbent were equilibrated with 300mL of various concentrations of Cu^{II}, Ni^{II} and Co^{II} for 2h. The concentrations were increased until a plateau value was obtained due to saturation. The adsorption capacity of various metal ions may differ due to their size, degree of hydration, and the value of their binding constant with the adsorbents. The static adsorption capacities were found as 67.1, 52.9 and 64.4 mg g⁻¹ for Cu^{II}, Ni^{II} and Co^{II} respectively. Reusability is another key factor for evaluating the performance of an adsorbent. Thus, the reusing ability of the adsorbent in several successive extraction processes was examined. The obtained results showed that the magnetic adsorbents can be reused for five times (RSD/43.7%) without sacrificing adsorption efficiencies.

3.7. Analytical Performance

Optimized experimental conditions were employed to evaluate the analytical performance of the proposed method. The linear dynamic range was obtained between 0.01 and 750 ngmL⁻¹ with preconcentration of target analyte ions with appropriate correlation coefficients (r²>0.999). The limit of detection (LOD) of the proposed method was obtained based on three times of the blank standard deviation (3S_b) for seven replicates of the blank analysis according to the following equation: LOD = 3/3S_b=m where S_b is the standard deviation of the y-intercept of regression line and m is the slope of the calibration curve. Under the optimized conditions, the LODs were 5, 7 and 2 ngL⁻¹. The experimental preconcentration factor were found as 291, 285, and 288 and the relative standard deviation (RSD) for the

determination of 50 ng mol L⁻¹ of each metal ion 3, 7, and 3 ng L⁻¹ for Cu^{II}, Ni^{II} and Co^{II}. The reported method showed very high preconcentration factors and low detection limits in a very short analysis time attributing to the large surface area, strong magnetism, and rapid extraction dynamics of thiodiethanethiol grafted tetraethyl orthosilicate modified magnetic nanoparticles adsorbent.

3.8. Application

The applicability of the proposed method was examined by application to tap water and canned Mosu fish samples. The obtained results are summarized in Table 3. As can be seen, the recoveries were in the range of 95–100% indicating that the method is applicable for the determination of ngmL⁻¹ levels of Cu^{II}, Ni^{II} and Co^{II} in water and food samples with good accuracy. Furthermore, the analytical procedure was validated by analysis of a certified reference material. The results revealed good agreement between the obtained values and certified values Table 4. These results confirm the validity of the proposed method for the preconcentration of the metal ions from aqueous matrices.

Table 1. ICP-OES: operating conditions and selected emission lines

Parameters	
RF Power (KW)	1.0
Nebulizer pressure (bar)	3.0
Plasma gas flow (l min ⁻¹)	16
Auxiliary gas flow (l min ⁻¹)	1.7
Sample uptake rate (ml min ⁻¹)	0.8
Stabilization time (s)	15
Read time (s)	1
Emission lines (nm)	
Cu	324.754
Ni	232.003
Co	237.862

Table 2. Effect of Co-existing ions the recovery of Cu^{II}, Ni^{II} and Co^{II} ions using the batch extraction method

Interference	Tolerance ratio (w/w)	Found (ng mL ⁻¹)		
		Cu ^{II}	Ni ^{II}	Co ^{II}
Li ⁺ , Na ⁺ , K ⁺ , Mg ⁺² , Ca ⁺²	18000	98±2	99±2	95±2
Ba ⁺² , Mn ⁺² , Sr ⁺²	4000	95±2	97±2	97±2
Fe ⁺³ , Cr ⁺³ , Al ⁺³	1000	98±2	96±2	97±2
Zn ⁺²	400	96±2	98±2	98±2
Cl ⁻	800	96±2	98±2	98±2
NO ₃ ⁻ , SO ₄ ⁻² , PO ₄ ⁻³	10000	96±2	98±2	96±2

Table 3. Determination of trace metal ions in various water samples

Elements	Added (µg)	River water ^b		Added (µg)	Mosu Fish ^c	
		Found (µg/ml)	Recovery (%) ^a		Found (µg/ml)	Recovery (%)
Cu(II)	0	4.8	--	0	2.3	--
	5.0	9.6	96.0±0.2	5.0	7.0	96.0±0.8
	15.0	19.4	99.4±0.3	15.0	21.3	97.0±0.2
Ni(II)	0	0.4	--	0	2.4	--
	5.0	5.2	98.0±0.6	5.0	7.2	92.0±0.3
	15.0	15.4	97.3±0.2	15.0	20.4	99.0±0.2
Co(II)	0	0.5	--	0	1.2	--
	2.5	2.9	96.0±0.4	5.0	3.6	96.0±0.2
	5.0	5.2	94.0±0.2	15.0	6.1	98.0±0.6

^aMean standard deviation(n=5), ^bCollected from Penna river (Nellore), ^cCollected from Bay of Bengal (Nellore, A.P. India)

Table 4. Determination of Cu^{II}, Ni^{II} and Co^{II} in certified reference material (IAEA-407)

Element	Certified (µg/g) ^a	Found (µg/g) ^b	RSD (%)
Cu ^{II}	3.28	3.21 ± 0.02	0.1
Ni ^{II}	0.60	0.62 ± 0.01	0.2
Co ^{II}	0.10	0.08 ± 0.04	0.6

Note: ^a The composition of the tissue powder (IAEA-407): Fe 146, Ni 0.6, Cu 3.28, Pb 0.12, Zn 67.1, Cd 0.189, Cr 0.73, Co 0.10 and Mn 3.52 (µg/g).

^b Mean of five determination at 95% confidence level ($\bar{x} \pm ts N$).

4. Conclusion

A sensitive, simple, and inexpensive magnetic batch extraction preconcentration technique was developed for the determination of Cu^{II}, Ni^{II} and Co^{II} at ultra-trace levels in environmental and food samples using magnetic nanoparticles which were coated with tetraethyl ortho silicate and modified with thio diethanethiol as adsorbents. For metal ions, the detection limits were obtained in the 2–8 ng L⁻¹ range (concentration 50 ng mL⁻¹, n^o/47). The magnetic extraction procedure was shown to have major advantages over the traditional micronized sorbent materials such as low time consumption due to magnetically assisted separation procedure, low adsorbent usage because of higher surface area of magnetic nanoparticles, and easy adsorbent generation through a simple chemical co-precipitation method. The method can successfully apply to the extraction and preconcentration of the analytes in tap water and canned Mosu fish samples.

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REFERENCES

- Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q.; *J. Hazard. Mater.* 2012, 317,211.
- Xu, P.; Zeng, G.M.; Huang, D.L.; Feng, C.L.; Hu, S., Zhao, M.H.; Lai, C.; Wei, Z.; Huang, C.; Xie, G.X.; Liu, Z.F.; *Sci. Total Environ.* 2012, 424, 1.
- Li, L.; Fan, M.H.; Brown, R.C.; Van Leeuwen, J.H.; Wang, J.J.; Wang, W.H.; Song, Y.H.; Zhang, P.Y.; *Crit. Rev. Environ. Sci. Technol.* 2006, 36, 405.
- Wei, L.; Yang, G.; Wang, R.; Ma, W.; *J. Hazard. Mater.* 2009 164, 1159.
- Hu, J.; Chen, G.H. Lo, I.M.C.; *Water Res.* 2005, 39, 4528.
- Hu, J.; Chen, G.H.; Lo, I.M.C.; *J. Environ. Eng.-ASCE.* 2006, 132, 709.
- Tuzen, M.; *Food Chem Toxicol.* 2009, 47(8), 1785.
- Tangjuank, S.; Insuk, N.; Tontrakoon, J.; Udeye, V.; *World Academy of Science, Engineering and Technology*, 2009, 28, 110.
- Fu, F.; Wang, Q.; *A review. Journal of Environmental Management.* 2011, 92(3), 4078.
- Parham, H.; Zargar, B.; and Shiralipour, R.; *J. Hazard. Mater.* 2012, 205–206, 94.
- Guihen, E.; and J. D.; Glennon. *Anal. Lett.* 2003, 36, 3309.
- Yuwei, C.; and Jianlong, W.; *Chem. Engin. J.* 2011, 168(1), 286.
- Faraji, M., Saleh, A.; Rezaee, M.; Ghambarian, M.; and Hassani, R. *Anal. Chim. Acta.* 2010, 659, 172.

14. Wang, Y.; Luo, X.; Tang, J.; Hu, X.; Xu, Q.; and Yang, C. *Anal. Chim. Acta*, 2012, 713,92.
15. Huang,C.; and Hu. B.; *Spectrochim. Acta B*, 2008, 63, 437.
16. Zhang, J.; Ding, J.; Yin, T.; Hu, X.; Yu, S.; and Qin,W.; *Talanta*, 2010, 81(3), 1056.

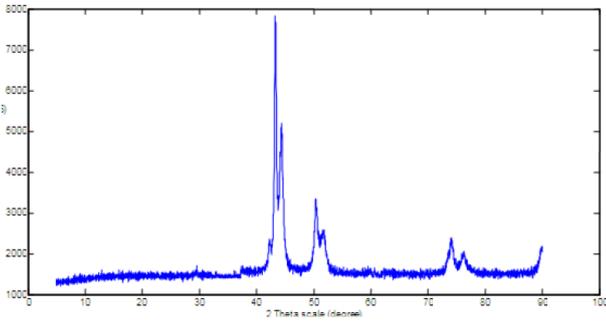


Figure 1 (a) XRD pattern of Cu^{II},Ni^{II} and Co^{II} nano particle.

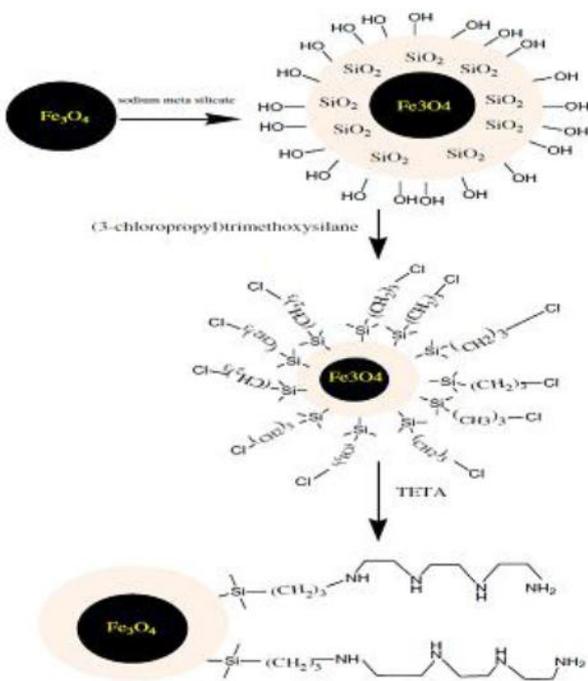


Figure 1(b). Synthetic route of nano sorbents

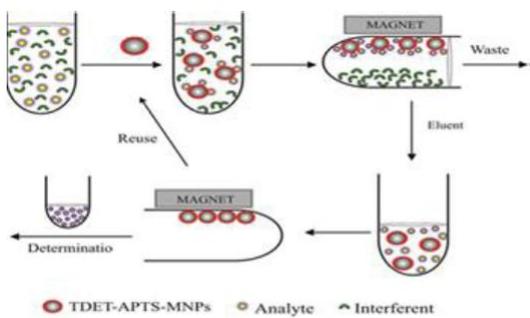


Figure 2. Preconcentration (Solid Phase Extraction) Procedure

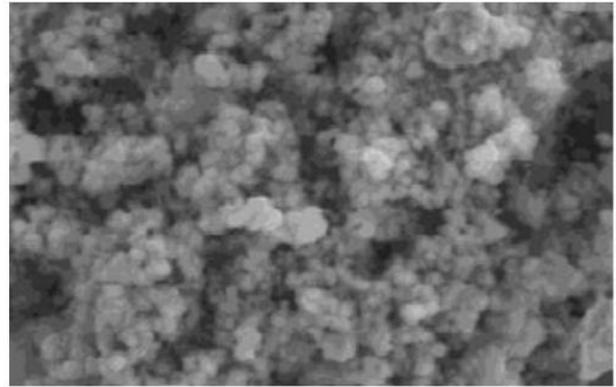


Figure 3. Sem Image of the Nano Particle

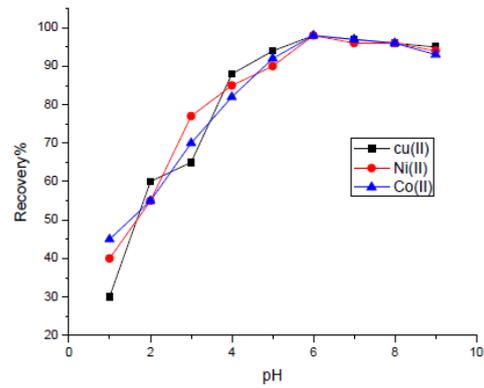


Figure 4. Effect of pH =6 on the recovery of metal ions

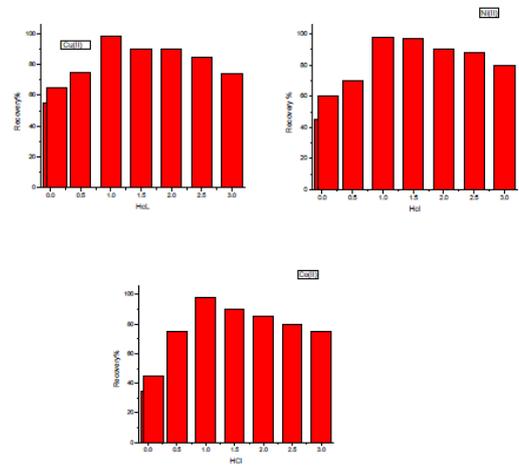


Figure 5. Effect of various eluents on the recovery of Cu^{II}, Ni^{II} and Co^{II}; pH 6; sample volume 300 mL, and the amount of the adsorbent was 85 mg.

17. Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q.; *J. Hazard. Mater.* 2012, *317*, 211.
18. Xu, P.; Zeng, G.M.; Huang, D.L.; Feng, C.L.; Hu, S., Zhao, M.H.; Lai, C.; Wei, Z. ; Huang, C.; Xie, G.X.; Liu, Z.F.; *Sci. Total Environ.* 2012, *424*, 1.
19. Li, L.; Fan, M.H.; Brown, R.C.; Van Leeuwen, J.H.; Wang, J.J.; Wang, W.H.; Song, Y.H.; Zhang, P.Y.; *Crit. Rev. Environ. Sci. Technol.* 2006, *36*, 405.
20. Wei, L.; Yang, G.; Wang, R.; Ma, W.; *J. Hazard. Mater.* 2009 *164*, 1159.
21. 5 Hu, J.; Chen, G.H. Lo, I.M.C.; *Water Res.* 2005, *39*, 4528.
22. Hu, J.; Chen, G.H.; Lo, I.M.C.; *J. Environ. Eng.-ASCE.* 2006, *132*, 709.
23. Tuzen, M.; *Food Chem Toxicol.* 2009, *47(8)*, 1785.
24. Tangjuank, S.; Insuk, N.; Tontrakoon, J.; Udeye ,V.; *World Academy of Science, Engineering and Technology*, 2009, *28*, 110.
25. Fu, F.; Wang, Q.; A review. *Journal of Environmental Management*, 2011, *92(3)*, 4078.
26. Parham, H.; Zargar, B.; and Shiralipour, R.; *J. Hazard. Mater.* 2012, *205–206*, 94.
27. Guihen, E.; and J. D.; Glennon. *Anal. Lett.* 2003, *36*, 3309.
28. Yuwei, C.; and Jianlong, W.; *Chem. Engin. J.* 2011, *168(1)*, 286.
29. Faraji, M., Saleh, A.; Rezaee, M.; Ghambarian, M.; and Hassani. R. *Anal. Chim. Acta*, 2010, *659*, 172.